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The role of the symmetry and the flexibility of the anion on the characteristics of the nanostructures and the viscosities of ionic liquids☆



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ABSTRACT

The transport properties of ionic liquids (ILs) are crucial properties in view of their applications in electrochemical devices. One of the most important advantages of ILs is that their chemical–physical properties and consequently their bulk performances can be well tuned by optimizing the chemical structures of their ions. This will require elucidating the structural features of the ions that fundamentally determine the characteristics of the nanostructures and the viscosities of ILs. Here we showed for the first time that the “rigidity”, the order, and the compactness of the three-dimensional ionic networks generated by the anions and the cation head groups determine the formation and the sizes of the nanostructures in the apolar domains of ILs. We also found that the properties of ionic networks are governed by the conformational flexibility and the symmetry of the anion and/or the cation head group. The thermal stability of the nanostructures of ILs was shown to be controlled by the sensitivity of the conformational equilibrium of the anion to the change of temperature. We showed that the viscosity of ILs is strongly related to the symmetry and the flexibility of the constitute ions rather than to the size of the nanostructures of ILs. Therefore, the characteristics of the nanostructures and the viscosities of ILs, especially the thermal stability of the nanostructures, can be fine-tuned by tailoring the symmetry and the conformational flexibility of the anion.

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1. Introduction

Ionic liquids (ILs) are the molten salts that generally consist of bulky organic cations paired with anions such as BF_4^- , PF_6^- , and Tf_2N^- (bis(trifluoromethylsulfonyl)imide) [1–5]. A unique feature of ILs is the presence of nanostructures, in which the anion and the cation head group form three-dimensional ionic networks, and the cation chains segregate into nonpolar domains that are embedded into three dimensional ionic networks. The formation of nanostructures fundamentally changes the properties of ILs [3,4,6–10] and makes the ILs very attractive solvents for electrochemical devices [11–14] and photoelectrochemical solar cells [15]. Of course, a suitable exploitation of the performance of ILs requires a deep knowledge of the effect of their architectures on the chemical–physical properties. Recognition of the nanostructures of ILs is essential for systematic interpretations of the properties of ILs [3,6–10,16–18], especially the transport properties (viscosity, diffusion, and electrical conductivity) of ILs [3,6–10,16,17].

The existence of nanostructures in ILs has been identified by a wide variety of methods, including MD simulations [16,19,20], Raman

spectroscopy [21,22], X-ray diffraction [23], small-wide angle X-ray scattering (SWAXS), femtosecond optical heterodyne-detected Raman-induced Kerr effect spectroscopy (OHD-RIKES) [24], Neutron spin echo (NSE) [25], etc. However, these studies are focused on the influence of the cation chain length on the characteristics of the nanostructures of ILs [18,20,23,26]. The effect of the anion on the features of the nanostructures of ILs, especially the underlying mechanism, is seldom addressed. This is inconsistent with the fact [3,7–10,16,18,20] that the nature of the anion exerts a significant influence on the transport properties of ILs. In addition, the relationship between the characteristics of the nanostructures of ILs and their transport properties is poorly understood.

In this study the freeze-fracture transmission electron microscopy (FF-TEM) measurements were made for the first time to investigate the nanostructures of the typical ILs. In addition, such investigations were not limited to the influence of the cation chain length on the characteristics of the nanostructures of ILs. The dependence of the features and the thermal stability of the nanostructures of ILs on the symmetry and the conformational flexibility of the anion was elucidated for the first time. The structural features of the constitute ions that fundamentally determine the characteristics of the ionic networks and the nanostructures of ILs were also identified. The efforts were made to see whether or not the viscosity of ILs is related to the size of their nanostructures. These results are important for the applications of ILs in electrolytic conductor and chemical reactions and phase equilibrium [12].

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2. Experimental

2.1. Preparation of ionic liquids

$[\text{C}_n\text{mim}][\text{Tf}_2\text{N}]$ ($n = 4$ and 6) and $[\text{C}_n\text{mim}][\text{PF}_6]$ ($n = 4, 6,$ and 8) were supplied by Merck with the claimed purity of $\geq 99.0\%$. They were dried in vacuo at 323 K for several hours before use. These ILs were further dried with 0.3 nm molecular sieve for days immediately before use. The water content after drying, measured by Karl Fisher titration, was $\leq 0.02\%$ (by mass).

2.2. The freeze-fracture transmission electron microscopy (FF-TEM) measurements

The procedure is as follows. The samples were injected into the sample holders (gold stub of sample carriers for knife fracture). For temperature tests, the holders with samples were placed into an oven at the desired temperature; for cryogenic tests, they were put into the chamber of the freeze substitution device (Leica AFS2) maintained at the desired temperature. In both cases more than half an hour was used to achieve thermal equilibrium. Then, the samples in the holders were immersed rapidly into liquid ethane cooled in advance with liquid nitrogen. Subsequently, they were rapidly transferred into liquid nitrogen.

The samples put into the chamber of the freeze-etching apparatus (BALZERS BAF-400 D) were fractured at 150 K at a pressure of $3 \times 10^{-5}\text{ Pa}$. After being etched, Pt-C was sprayed onto the fracture face at 45° until it reached 20 nm thickness, and then C was sprayed at 90° with 150 nm thickness. The coated samples (in replicate) were removed from the chamber and were dipped into dimethyl benzene. Then, these coated samples were washed with ethanol and doubly distilled water, respectively. The replicate samples were mounted onto grids and viewed with a transmission electron microscope (PHILIPS-FEI TECNAI20).

2.3. The Raman spectra measurements

The Raman spectra were obtained using a HR800 micro-Raman spectrometer (Jobin Yvon, France) employing a 785 nm laser beam, with an instrument resolution of 0.5 cm^{-1} . Sample temperatures were controlled using a Linkam TS600 hot stage with a temperature stability of $\pm 0.5\text{ K}$. The temperature was held fixed for at least 5 min at each selected temperature in order to get a more accurate and stable sample temperature. The Raman spectra were measured in both crossed $Z(XY)\bar{Z}(VH)$ and parallel $Z(XY)\bar{Z}(VV)$ polarizations, where $X, Y,$ and Z are the cubic axes. The temperature was measured with a PT100 with an evaluating standard uncertainty of $\pm 0.006\text{ K}$.

3. Results and Discussion

3.1. Influence of the anionic structure on the formation of nanostructures in typical ionic liquids

The present measurements were made at three temperatures ($193, 298,$ and 353 K). The FF-TEM images of the nanostructures formed in $[\text{C}_n\text{mim}][\text{PF}_6]$ and in water are shown in Fig. 1. As expected, no nanostructure was detected in water. It is seen that the changes in the number, the size, and the compactness of the FF-TEM nanostructures are more remarkable on going from $n = 4$ to $n = 6$ than on going from $n = 6$ to $n = 8$. In addition, the FF-TEM nanodomains are less extensive in $[\text{C}_4\text{mim}][\text{PF}_6]$ than in $[\text{C}_6\text{mim}][\text{PF}_6]$ and $[\text{C}_8\text{mim}][\text{PF}_6]$. The FF-TEM images of the nanostructure formed in $[\text{C}_n\text{mim}][\text{Tf}_2\text{N}]$ are shown in Fig. 2. There exist extensive nanostructures in $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ at 193 K . However, these nanostructures are apparently softening with increasing the temperature and most nanostructures have “melted” at 298 K .

In the case of $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$, the nanostructures are extensive at 193 and 298 K but “melt” at 353 K .

In order to explore the structural factors that dominate the formation of the nanostructures in the above-mentioned ILs, we measured the Raman spectra for these ILs. As is seen from Fig. 3, the variation of the intensity of the Raman bands of the cation conformers of all the examined ILs with temperature is very small. However, the intensities of the Raman bands of the C_1 conformer relative to those of the Raman bands of the C_2 conformer of the Tf_2N^- anion in $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ significantly increase as the temperature increases from 183 to 355 K , indicating that the conformational disorder of the anion is considerably promoted [3,27] as the nanostructures were “melted” at 298 K . PF_6^- is highly symmetric and Fig. 4 shows that the changes in the relative intensities of the Raman bands of both C_6mim^+ and PF_6^- are negligibly small when the temperature is increased from 190 to 355 K . As seen from Fig. 1, all the PF_6^- -based ILs examined herein contain extensive nanostructures even at 353 K and, more remarkably, these nanostructures show much less temperature dependence than the nanostructures of $[\text{C}_n\text{mim}][\text{Tf}_2\text{N}]$ in the 193 – 353 K temperature range. This means that the thermal stability of the nanostructures strongly correlates with the thermal changeability of the conformation equilibrium of the anion and that the effect of the anion overrides that of the cation chain length.

The finding that the characteristics of the nanostructures of ILs are dominated or at least strongly related to the nature of the anion is important. It is useful for us to understand the complex behavior of ILs. For example, it is found that $[\text{C}_4\text{mim}][\text{PF}_6]$ behaves nearly like a normal Gaussian fluid at 500 K , whereas there is a large deviation from Fickian behavior at 300 K [18]. Our measurements cannot be conducted at sufficiently high temperature to detect the “melting” temperatures of the tail domains of $[\text{C}_n\text{mim}][\text{PF}_6]$. However, it is reasonable to attribute the Gaussian behavior of $[\text{C}_4\text{mim}][\text{PF}_6]$ at 500 K to the “fusion” of the nanostructures of $[\text{C}_4\text{mim}][\text{PF}_6]$ at 500 K . In addition, the anion-dependence of the thermal stability of the nanostructures of $[\text{C}_n\text{mim}][\text{PF}_6]$ and $[\text{C}_n\text{mim}][\text{Tf}_2\text{N}]$ can explain why the temperature dependence of the OKE spectra of ILs is controlled by the nature of the anion [28].

3.2. Is the viscosity of ionic liquids dominated by the size of the nanostructures?

It can be seen from Figs. 1 and 2 that the size of the nanostructures formed in the ILs considered increases apparently with increasing temperature. In general, the size of the nanostructures derived from FF-TEM ranges from 15 to 40 nm at 193 and 298 K , in consistency with the results obtained from CARS signals [21]. The spatial distribution measurement of CARS signals indicate that local structures formed in $[\text{C}_n\text{mim}][\text{PF}_6]$ ($n = 4, 6,$ and 8) is most likely to be several tens of nanometers [21]. The size of nanostructures of ILs derived either from FF-TEM or from SWAXS [24] increases with increasing the cation chain length and increases from Tf_2N^- to PF_6^- . For the purpose of comparison, the results reported in refs. [24] and [29] (see Table 1) were invoked to study the effect of the size of nanostructures on the viscosity of ILs.

The SWAXS results [24] show that the size of the nanostructures of the ILs based on C_6mim^+ or C_8mim^+ at 298.15 K increases in the order $\text{Tf}_2\text{N}^- < \text{PF}_6^- < \text{BF}_4^-$ (also see Table 1). However, the viscosity of the C_6mim^+ -based ILs in the 298 – 353 K temperature range increases with increasing the rigidity and the symmetry of the anion in the order $\text{Tf}_2\text{N}^- < \text{BF}_4^- < \text{PF}_6^-$ [6,30–32]. The viscosity of the C_8mim^+ -based ILs at 293.15 K also increases from $[\text{C}_8\text{mim}][\text{Tf}_2\text{N}]$ through $[\text{C}_8\text{mim}][\text{BF}_4]$ to $[\text{C}_8\text{mim}][\text{PF}_6]$ [29,33]. These comparisons show that the viscosity of ILs is not dominated by the size of the nanostructures of ILs.

The SWAXS results [29] show that the size of the nanostructures increases considerably from $[\text{PIP}_{1,n}][\text{Tf}_2\text{N}]$ ($\text{PIP}_{1,n}$ is the N -methyl- N -alkylpiperidinium cation with $5 \leq n \leq 7$) to $[\text{C}_n\text{mim}][\text{Tf}_2\text{N}]$. However, the

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